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ATTORNEY'S DOCKET NUMBER
UC17974-1

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (if known: see 37 C.F.R. 1.5)

10/031244

INTERNATIONAL APPLICATION NO.
PCT/US00/10512

INTERNATIONAL FILING DATE
19 April 2000

PRIORITY DATE CLAIMED
20 April 1999

TITLE OF INVENTION
PIGMENTED COMPOSITIONS

APPLICANT(S) FOR DO/EO/US

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Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☒ is not required, as the application was filed in the United States receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the Annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 15. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ A FIRST preliminary amendment.
- ☐ A SECOND or SUBSEQUENT preliminary amendment.
13. ☐ A substitute specification.
14. ☐ A change of power of attorney and/or address letter.
15. ☐ Other items or information:

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.50) <div style="font-size: 1.5em; font-weight: bold; margin-top: 5px;">10/031244</div>	INTERNATIONAL APPLICATION NO. PCT/US00/10512	ATTORNEY'S DOCKET NUMBER UC17974-1
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17. <input checked="" type="checkbox"/> The following fees are submitted: <div style="margin-top: 10px;"> Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO \$ 890.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) \$ 710.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$ 740.00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445 (a)(2)) paid to USPTO \$ 1,040.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$ 100.00 </div> <div style="text-align: right; margin-top: 5px;"> ENTER APPROPRIATE BASIC FEE AMOUNT = </div>	CALCULATIONS	PTO USE ONLY
Surcharge of \$ 130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	+	\$ 130.00

Claims	Number Filed	Number Extra	Rate		
Total Claim	15 - 20 =	0	X \$ 18.00	\$ 0.00	
Independent Claims	1 - 3 =	0	X \$ 84.00	\$ 0.00	
Multiple dependent claim(s) (if applicable)			\$ 0.00	\$ 0.00	

Processing fee of \$ 0 for furnishing the English Translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).	+	\$ 0.00
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\$ 1,020.00		

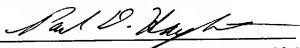
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a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.

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Note: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO: Graham E. Taylor The Dow Chemical Company Intellectual Property P.O. Box 1967 Midland, Michigan 48641-1967 UNITED STATES OF AMERICA	Signature: <u></u> <div style="text-align: center; margin-top: 5px;"> Paul D. Hayhurst , Registration No. 30,180 </div> Date: <u>19 October 2001</u>
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PIGMENTED COMPOSITIONS

Field of the Invention

The present invention relates to polymer-containing pigment compositions, e.g., ink compositions, suitable for decorative and protective coatings for rigid and flexible substrates. More specifically, the present invention relates to polymers suitable for use as binders in such pigmented compositions.

Background of the Invention

Pigments are often used in industry to impart color to coatings applied to rigid and flexible substrates, e.g., in packaging. As used herein the term "pigment" means a particulate material that can impart color to another substance or mixture. In general, the pigments are insoluble in aqueous or organic liquids, the coloring effect being a result of their dispersion in a solid or liquid medium.

In order to form smooth, high gloss coatings, pigments must be well dispersed in a liquid medium, e.g., ink formulation, and must be resistant to agglomeration. Agglomerated pigment particles can cause a rough, bumpy appearance on coated substrates, which is generally believed to be undesirable. In order to avoid agglomeration, pigments are typically ground, e.g., milled, with a polymer used for binding the pigment particles to the substrate to be coated either alone or along with a solvent for the binder polymer.

Improved pigment compositions comprising pigment particles and a polymer suitable for binding the pigment particles to a substrate to be coated are desired. It is further desired that the binder polymers utilized in such compositions would be effective to inhibit the agglomeration of the pigment particles in the liquid medium in which they are dispersed.

Summary of the Invention

In accordance with the present invention, improved pigment compositions are provided which comprise pigment particles and a binder polymer which is effective to inhibit the agglomeration of the pigment particles when dispersed in a liquid medium. The compositions of the present invention can be provided as a dispersion of the pigment particles in a liquid medium having dissolved therein the binder polymer or as a solid composition of the binder polymer and the pigment particles.

By virtue of the present invention, it is now possible to avoid large viscosity increases of typical pigment compositions which can be caused during the grinding of the pigment particles and the binder polymer. The pigment compositions of the present invention can provide a smaller ultimate pigment particle size than obtained in conventional pigment dispersions, low viscosities even at high solids content, high gloss values in short grinding times and good thermal stability.

Detailed Description

The particular pigment particles used in accordance with the present invention are not critical. Typically, the pigment particles have a particle size, before grinding of from about 5 to 50 microns. Most pigments are insoluble in organic solvents and water. Exceptions are natural organic pigments, such as, chlorophyll, which are generally organosoluble. In general, the pigments may be classified as follows.

I. Inorganic

- A. Metal oxides, e.g., iron, titanium, zinc, cobalt and chromium;
- B. Metal powder suspensions, e.g., gold and aluminum;
- C. Earth colors, e.g., siennas, ochers, umbers;
- D. Lead chromates; and
- E. Carbon black.

II. Organic

- A. Animal, e.g., rhodopsin, melanin;
- B. Vegetable, e.g., chlorophyll, xanthophyll, indigo, flavone, carotene;
- C. Synthetic, e.g., phthalocyanine, lithos, toluidine, para red, toners, lakes.

The compositions of the present invention typically comprise from about 1 to 99 weight percent, preferably from about 1 to 80 weight, percent based on the total weight of the composition of the pigment particles. Further details concerning suitable pigments are known to those skilled in the art. Such pigments are readily commercially available.

The polymers suitable for use in accordance with the present invention are polymers which are effective to inhibit the agglomeration of the pigment particles when dispersed in a liquid medium.

A typical polymer suitable for use in accordance with the present invention is a copolymer polymerized from the following monomeric moieties. As used herein, the term "copolymer" means a polymer made from two or more monomers.

- (a) a first monomeric moiety of a vinyl halide, e.g., vinyl chloride of the formula $\text{—CH}_2\text{—CHCl—}$, preferably from 50 to 95 percent by weight;

- 4 -

(b) a second monomeric moiety of a monoethylenically unsaturated monomer different from components (a), (c), and (d), preferably a vinyl ester, e.g., vinyl acetate of the formula $\text{—CH}_2\text{—CH(O—CO—CH}_3\text{)—}$, preferably from 2 to 30 percent by weight;

(c) a third monomeric moiety of a sulfur-bearing acrylate or methacrylate, e.g., sulfoethylmethacrylate or a metal or amine salt thereof, preferably from 0.1 to 5 percent by weight; and

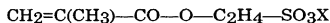
(d) optionally a fourth or more monomeric moieties of one or more monoethylenically unsaturated monomers different from components (a), (b) and (c), preferably from about 0 to 20 percent by weight.

The vinyl halide monomers suitable for use in accordance with the present invention include vinyl chloride, vinyl bromide and vinyl fluoride, with vinyl chloride being preferred. Such vinyl halide monomers are commercially available. The amount of vinyl halide monomer used in the copolymers of the present invention is typically from about 50 to 95 weight percent, preferably from about 55 to 80 weight percent and more preferably from about 60 to 75 weight percent, based on the total weight of the monomers in the copolymer.

The vinyl ester monomers suitable for use in accordance with the present invention include those having from 2 to about 16 carbon atoms in the ester group. Suitable vinyl ester monomers include, for example, vinyl acetate, vinyl propionate, vinyl butyrates, vinyl pentanoates, vinyl neopentanoate, vinyl hexanoates, vinyl octanoates, vinyl 2-ethylhexanoate, vinyl nonanoates, vinyl decanoates, vinyl neoanoates, vinyl neododecanoate, and the like. Preferred vinyl esters are vinyl acetate and vinyl propionate, and the most preferred vinyl ester is

vinyl acetate. The vinyl esters suitable for use in accordance with the present invention, are commercially available. The amount of vinyl ester monomer in the copolymers of the present invention is typically from about 2 to 30 weight percent, preferably from about 3 to 15 weight percent, and more preferably from about 5 to 12 weight percent, based on the total weight of the monomers in the copolymer.

The third monomeric moiety is preferably sulfoethylmethacrylate either in the free acid form or in the salt form with a metallic element or an amine. In this regard, the weight fraction thereof should be at least 0.1 percent although an excessively large weight fraction thereof over 5 percent has no particularly advantageous effect. The monomeric moiety of this type can be introduced into the polymeric resin by the copolymerization of sulfoethylmethacrylate or derivative having an ethylenically unsaturated polymerizable group and a sulfonic acid group $\text{—SO}_3\text{X}$ in which X is a hydrogen atom, an atom of a metal such as alkali metals, or a protonated amine. Examples of suitable sulfoethylmethacrylate monomers or derivatives include those expressed by the following structural formula, in which X is an atom of hydrogen, an alkali metal e.g., sodium and potassium, or a protonated amine:



Other sulfur containing monomers include, for example, 2-acrylamido-2-methyl propanosulfonic acid, and sulfomethylmethacrylate.

The copolymers of the present invention may comprise other monomers in addition to the monomers described above. Such additional monomers include, for example, other vinyl monomers having from 2 to 10 carbon atoms per molecule,

acrylates or methacrylates having from 3 to 20 carbon atom per molecule, acrylonitriles, methacrylonitriles, and the like.

Illustrative of the other vinyl monomers include, for example, maleic anhydride, maleic acid, fumaric acid, itaconic acid and itaconic anhydride, and maleate, fumarate and itaconate diesters and half esters, vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, propyl vinyl ethers, vinyl alcohol that is formed from the hydrolysis of vinyl esters such as vinyl acetate, and the like. Preferred optional vinyl monomers are maleic acid and maleic anhydride.

Illustrative of the acrylates and methacrylates are acrylic acid, methacrylic acid, the esters of acrylic and methacrylic acid such as, for example, methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl, and the like, e.g., bornyl, isobornyl and isonorbornyl acrylate; 3-hydroxy-1-isopropyl-2,2-dimethylpropyl-(meth)acrylate, 3-hydroxy-2,2,4-trimethylpentyl (meth)acrylate, dicyclopentenylacrylate; hydroxyethyl acrylate, hydroxyethyl methacrylates, hydroxypropyl acrylate, hydroxypropyl methacrylates, hydroxyhexyl acrylates, hydroxydecyl acrylates; caprolactone acrylates, cyclohexyl acrylate, 2-phenoxyethyl acrylate, glycidyl acrylate, glycidyl methacrylate, and the like. Preferred acrylates are hydroxypropyl acrylate and glycidyl methacrylate.

The amount of the additional monomers, when employed in the copolymers of the present invention, is typically from about 0.5 to 30 weight percent and preferably from about 1 to 20 weight percent, based on the total weight of the monomers and the copolymer. Further details concerning the selection, preparation, availability and amounts of the additional monomers are known to those skilled in the art.

Suitable copolymers include, for example, those described in U.S. Patent Nos. 4,707,411 and 5,531,914. Such copolymers are commercially available, for example, from Union Carbide Corporation, Danbury, CT (sold as UCARMAG™569) and Nippon Zeon Co., Ltd., Tokyo, Japan (sold as MR-110).

The copolymer preferably has an average degree of polymerization in the range from 200 to 800. When the average degree of polymerization thereof is too small, no sufficiently high mechanical strengths as well as durability can be imparted to the compositions formulated with the copolymer. When the average degree of polymerization thereof is too large, the coating composition formulated with the copolymer in a desired concentration may have an increased viscosity to badly affect the workability with the composition. Those skilled in the art can determine the suitable degree of polymerization.

The copolymerization reaction of the comonomers can be performed by any known method including the methods of suspension polymerization, emulsion polymerization, solution polymerization, bulk polymerization and the like.

Conventional solution polymerization techniques may be desirably utilized to form the binder polymers of this invention. Similarly, other polymerization techniques such as conventional suspension or emulsion polymerization may also be used. Thus, the process employed for making the resins of this invention is not critical, and such technology is well understood by those in the art. Suitable preparative techniques are, for example, set forth in U.S. 3,755,271.

In general, and as an illustrative example, the resins of this invention may be prepared by utilizing solution polymerization, employing a solvent for the resulting resin as well as for the various components employed. Suitable solvents include, for example, the conventional ester solvents such as butyl acetate, ethyl acetate,

isopropyl acetate, and the like, as well as the ketone solvents such as acetone, methyl ethyl ketone, methyl-n-butylketone, methyl-isopropylketone, and the like.

The polymerization may be carried out either batch-wise or continuously. Typically, the ratio of solvent/monomer will vary from about 0.3/1 to about 4/1, depending upon the molecular weight desired. The temperature selected may vary from about 35°C. to about 80°C., depending upon the reaction rate and resin molecular weight desired. Any oil-soluble, free radical catalyst may be used in an amount varying from about 0.01 to about 3.0%, based on the weight of the monomer. Suitable catalysts include, as illustrative examples, dibenzoyl peroxide, dilauroyl peroxide, azobisbutyronitrile and diisopropylperoxydicarbonate. Any pressure above the vapor pressure of the components of the system may be employed, pressures from about 30 to 100 psig being typical.

In the preparation of a composition by using the above-described specific copolymer as a vehicle of the pigment particles, the copolymeric resin can be used in combination with other polymeric resins conventionally used in the manufacture of pigmented compositions, usually in amounts of 50 percent by weight or less. Examples of polymers suitable for such a combined use include polyurethane resins, nitrocelluloses, epoxy resins, polyamide resins and phenolic resins as well as polymers and copolymers of acrylic and methacrylic acid esters, styrene, acrylonitrile, butadiene, ethylene, propylene, vinylidene chloride, acrylamide, vinyl ethers and the like.

In a preferred aspect of the invention, the composition will generally desirably include an elastomeric polymer in an amount sufficient to provide the composition with the desired properties. Many elastomeric polymers suitable for this purpose are known and may be utilized. Polyester urethanes are often preferred for high performance

applications. Suitable materials are commercially available. These materials may be, in general, described as the reaction products of polyester polyols, short chain diols, and isocyanates. These resins have excellent toughness and abrasion resistance characteristics.

A wide variety of polyisocyanate crosslinkers are known and may be used. Typically, polymeric polyisocyanates are employed. As one example, it is suitable to use polymeric toluene diisocyanate (TDI) adducts. The amount of crosslinking agent used is typically about 1 to about 25 percent by weight of the amount of vinyl halide copolymer and polyurethane in the formulation. A polyisocyanate crosslinker is typically used in formulations to improve properties such as hardness, tensile strength, glass transition temperature, etc. It is surprising that similar improvements are found in formulations containing the polymers described in this invention since these polymers contain no groups considered to be reactive towards isocyanates.

A variety of auxiliary agents are sometimes employed in the compositions. Such additives are known and may be employed, if desired for the particular application. For example, the compositions of the invention may be further admixed with various kinds of known additives conventionally used in pigment compositions including diluents, lubricating agents, dispersion aids, plasticizers, rust inhibitors, antistatic agents, leveling agents, wear resistant agents, film reinforcing agents and the like each in a limited amount. The compositions may be diluted with an organic solvent to impart an adequate viscosity or consistency suitable for the coating procedure. Examples of suitable organic solvents include methyl ethyl ketone, methyl isobutyl ketone, toluene and the like.

The particle size of the polymers of the present invention is typically from about 0.03 to 1.0 microns ("μ"), preferably from about 0.05 to 0.5 μ and more preferably from about 0.08 to 0.4 μ.

In accordance with the present invention, the polymers have an Inherent Viscosity of less than about 2.0, preferably from about 0.2 to 1.0 and more preferably from about 0.2 to 0.8. As used herein, the term "Inherent Viscosity" means the inherent viscosity determined using a Ubbelohde viscometer according to the ASTM D1243 procedure. Further details concerning the measurement of Inherent Viscosity are known to those skilled in the art.

The glass transition temperatures ("T_g") of the polymers of the present invention are typically at least about 40°C, preferably at least about 50°C and more preferably at least about 70°C.

The compositions of the present invention typically comprise from about 1 to 99 weight percent, preferably from about 20 to 99 weight percent, based on the total weight of the composition, of the polymer. Further details concerning suitable polymers are known to those skilled in the art. Such polymers are readily commercially available.

The compositions comprising the polymers of the invention have a variety of end uses, in general as pigment dispersions, ink compositions, coating compositions and adhesives. They can be formulated into products such as, for example, coatings (both rigid and flexible), sealants and adhesives. Further details concerning end uses, other ingredients typically contained in coating and adhesion formulations, such as, for example, surfactants, pigments, colorants, crosslinkers, e.g., phenolics, etc., are known to those skilled in the art.

For ink coatings in particular, pigment concentrates are commonly prepared with about a 1:1 weight ratio of pigment to binder polymer, with the addition of a suitable solvent, i.e., liquid medium, for the binder polymer. The pigment dispersions are typically prepared by

shearing or grinding the pigment and the polymer, e.g., a 3-roll mill or sand mill. The liquid medium can be provided in a low viscosity form to be pourable, e.g., water-like, or a high viscosity for, e.g., dough-like consistency, which would not flow except under shear. Likewise, the liquid medium can be provided in intermediate viscosity forms. The pigment compositions may also be provided in a solid form, e.g., a solid matrix of polymer and pigment (known in the art as a chip). In making the solid form of the composition, pigment can be added to the molten polymer of this invention on a heated heat two-roll mill or banbury mixer, or the like. Further details of such techniques are known to those skilled in the art. The pigment concentrate is often diluted with clear binder polymer solution to produce the required color hue and opacity needed for ink compositions. The diluted ink composition may contain a pigment to binder polymer solution ratio of as little as 0.1 or less.

The substrates to which the compositions can be applied are not limited and include, for example, wood, metal, glass, ceramic, plastic and paper.

The ink compositions prepared in the above described manner can be applied to the surface of a substrate in the form of films, tapes, sheets, foils, plates and the like of various kinds of materials without particular limitations including synthetic resins such as polyesters, polyolefins, cellulose acetates, polycarbonates and the like. The coating procedure with the ink or coating compositions can be performed by any known methods conventionally used to apply coatings and inks.

In one aspect of the invention, there is provided an ink composition which comprises from about 10 to 20 weight percent, e.g., about 15 weight percent, of the polymer of the present invention or combination thereof with another polymer, about 10 to 20 weight percent, e.g., about 13.5 weight percent, of a pigment, from about 2 to

10 weight percent, e.g., about 4.5 weight percent, of a plasticizer and from about 40 to 70 weight percent, e.g., about 48.0 weight percent methyl ethyl ketone and 19.0 weight percent methyl isobutyl ketone, of one or more solvents. Further details of ingredients contained in ink compositions and the amounts thereof are known to those skilled in the art.

In a preferred aspect of the invention, the pigment compositions can achieve high gloss levels, e.g., greater than 80, more preferably greater than 90, for a 60° gloss measurement using a 60° gloss meter with gloss readings taken on cast films on Leneta paper at 1:1 pigment to polymer ratio diluted to contain 50 weight percent cyclohexanone with grinding times of about 20 to 60 minutes. Moreover, preferably, the 60° gloss readings as described above are at least 60, more preferably at least 70, with a grinding time of 15 minutes or less.

In another preferred aspect of this invention, there is provided a solvent-free ink, coating, or casting. About 1 to 40 weight percent of the polymer of this invention is dissolved in about 60 to 90 weight percent of a strongly-solvating monomer such as, for example, methyl methacrylate, i.e., as the liquid medium, to form a syrup. A pigment, i.e., colorant is added and dispersed, e.g., milled, in the syrup. Syrups comprised of the polymer of this invention dissolved in acrylic monomers are often highly efficient in dispersing colorants. Another suitable monomer for this purpose is tetrahydrofural acrylate. Other suitable monomers can be determined by those skilled in the art.

In this aspect of the invention, the monomer is subsequently polymerized to form a solid alloy. Polymerization can be accelerated by addition of peroxide catalyst or the addition of a photoinitiator and exposure to ultraviolet light or electron beam radiation. Syrups containing about 20 to 30 percent of the polymer of this invention and 70 to 80 weight percent methyl methacrylate, preferably cure to a

water-clear solid having a single glass transition temperature, indicating excellent compatibility. Optionally, weakly-solvating monomers such as trimethylolpropane triacrylate can be used combinations with a strongly-solvating monomer such as methyl methacrylate. Syrups containing about 20 to 30 weight percent of the polymer of this invention in methyl methacrylate monomer typically have viscosity of 1400 to about 30,000 cP. at 25°C.

Examples

The following examples are representative of this invention, and not in limitation thereof. The following abbreviations were used in the examples:

VCl-vinyl chloride

VAc-vinyl acetate

SEMA-sulfoethyl methacrylate

HAA-hydroxyalkyl acrylate

VOH-vinyl alcohol

MA-maleic acid

AMPS-2-acrylamido-2-methylpropanesulfonic acid

MEK-methyl ethyl ketone

I.V.-Inherent Viscosity

EXAMPLE 1

General Polymerization Procedure - Vinyl Chloride Copolymers

The vinyl chloride copolymers were produced via continuous solution polymerization in a stainless steel stirred tank reactor. Vinyl chloride and the other monomers used, as well as the solvent, were pre-mixed and fed continuously to the reactor. The free radical initiator, diisopropylperoxydicarbonate, was also fed continuously as

- 14 -

an acetone solution, at a rate necessary to maintain constant conversion. Product solution was continuously withdrawn from the reactor. The temperature in the reactor was maintained at 50°C.-60°C. while the pressure was kept between 90-110 psig. The product solution was stripped of unreacted vinyl chloride monomer. Aqueous sodium carbonate was added to the acetone solution in a twofold excess based on the sulfonic acid. This converted the free sulfonic acid to the sodium salt prior to precipitation. The polymer was then recovered from solution by precipitation with an isopropanol/water mixture, filtered, and dried in a fluid bed drier.

Vinyl Chloride Copolymers

Weight Percent of Comonomer in Polymer

Polymers available from Union Carbide Corporation	VCI	Vac	SEMA	VOH	HAA	MA	I.V.
UCARMAG™ 569	85	13	2				0.40
UCAR™ VYHH	86	14					0.50
UCAR™ VAGH	90	4		6			0.53
UCAR™ VAGF	81	4			15		0.56
UCAR™ VMCH	86	13				1	0.50
UCARMAG™ 527 ¹	82	4			(14)		0.56

¹ Sum of HAA and MA equals 14 weight percent.

EXAMPLE 2

Preparation of Pigment Dispersions

Dry pigment was dispersed in solvent borne solutions of vinyl resins using the recipes shown in Table 1. The relative rate of dispersion was determined by gloss measurement and microscopic examination of thin cast films on glass plates.

The dry vinyl resin was first dissolved in MEK solvent. The resin solution was charged to a stainless steel beaker on a homo-dispersator. The dry pigment was added with slow agitation and allowed to wet out for five minutes. A portion of this mix was added to a stainless steel grinding vessel, together with an equal weight of zirconium oxide grinding media. The vessel contained equal volumes of liquid dispersion, media and head space.

Charged grinding vessels were placed in a holding block and agitated on a Red Devil paint shaker. Samples of the undiluted grind were taken after various time intervals and smeared on glass slides for microscopic measurement of particle size. Additional samples of grind were diluted 1:1 with cyclohexanone solvent and cast on Leneta paper for gloss measurement using a #12 wire wound rod. Cyclohexanone slows the drying rate and allows the film to level.

Table 1 shows that, when compared to pigment concentrates using other vinyl copolymers, lithol rubine red pigment dispersions containing Polymer 569 required significantly less grinding time to develop high gloss and develop a higher ultimate gloss. It is also shown that the rate of particle size reduction of the pigment was faster and the ultimate particle size was smaller.

Table 1
Gloss and Pigment Particle Size vs Grinding Time
Rubine Red Pigment Concentrates Prepared Using
Various Grinding Vehicles

Pigment Grind - Parts by Weight					
UCARMAG	15				
UCAR VYHH		15			
UCAR VYHH with added dispersant*			15		
UCAR VMCH				15	
UCAR VAGH					15
Rubine Red Pigment	15	15	15	15	15
methyl Ethyl Ketone	70	70	70	70	70
Total Grind	100	100	100	100	100
Cyclohexanone **	100	100	100	100	100

					<u>Comparative</u>
					<u>Values***</u>
Grinding time	20 ° Gloss				
5-min	17	5	6	coag.	4
25-min	45	14	10		13
55-min	54	18	15		19
Grinding time	60 ° Gloss				
5-min	54	28	30	coag.	24
25-min	97	56	48		52
55-min	103	67	59		67

15

60

TABLE 1 (Continued)

Grinding time	Average Particle Size (measurement microns)					2
5-min	3	5	12	coag.	5	
25-min	1	2	5		2	
55-min	1	2	2		2	

* 5% BK 101 based on pigment

** Post added to facilitate drawdown on Leneta paper

*** commercial Rubine red dispersion cut 1:1 with
cyclohexanone for gloss measurement

Table 2 shows that Lithol Rubine Red concentrates made using UCARMAG™ 569 exhibit uniquely low viscosity after grinding.

Carboxy-functional copolymer VMCH, which contains 1% maleic acid comonomer, had such high interaction with the rubine red pigment, that it coagulated when used as the sole polymer in the grinding medium. Other polymers produced substantially higher post-grind viscosity than UCARMAG™569. Accordingly UCARMAG™ 569 can offer manufactures of pigment concentrates improved productivity and cost savings.

TABLE 2
Effect of Polymer Composition in Grinding Vehicle

Pigment Grind - Parts by Weight					
UCARMAG™ 569	15				
UCAR VYHH		15			
UCAR VYHH with added dispersant*			15		
UCAR VMCH				15	
UCAR VAGH					15
Lithol Rubine Red Pigment	15	15	15	15	15
methyl Ethyl Ketone	70	70	70	70	70
	100	100	100	100	100
Viscosity before grinding, cP	54	94	124	Coag.	86
Viscosity after grinding 55 minutes cP	100	1200	810	-	1050

* 5% BK 101
 based on pigment
 Brookfield RVT Viscometer,
 100 rpm, 21 spindle

As used herein, the term "Viscosity" means the viscosity of a composition having 15 weight parts polymer, 15 weight parts Lithol Rubine Red Pigment and 70 weight parts Methyl Ethyl Ketone measured using a Brookfield RVT Viscometer with a No. 21 spindle at 100 RPM at 25°C. Preferably the Viscosity after grinding for 55 minutes is less than 700 cP, more preferably less than 200 cP. As used herein, the term "Viscosity Retention Factor" means the Viscosity measured after 55 minutes of grinding divided by the Viscosity

measured before grinding. Preferably, the Viscosity Retention Factor is about 5 or less, more preferably about 3 or less and most preferably about 2 or less.

Table 3 shows the viscosity and gloss properties of inks prepared by diluting the UCARMAG 569 /red pigment concentrate with various types of clear vinyl resin lacquers, each at 16% solids in MEK solvent.

In these examples, 3-parts of the UCARMAG 569 /red pigment concentrate was first diluted with 8-parts of UCARMAG 569 lacquer, followed by 8-parts of a second vinyl lacquer.

The ratio of UCARMAG 569 to other polymer was 57.5 to 42.5. A vehicle comprised of all-UCARMAG 569 was the benchmark: (3-parts of red concentrate diluted with 16 parts of UCARMAG 569).

In the second series of dilutions, 3-parts of the UCARMAG 569/red pigment concentrate was diluted with 16 parts of various vinyl lacquers, so that the ratio of UCARMAG 569 to other polymer was 15 to 85.

All of the resulting inks had a solids content of 18% and a pigment to binder ratio of 0.15.

TABLE 3
Properties of formulated inks

Pigment concentrate (30% solids ("nv")	Parts by Weight		
	3	3	3
UCARMAG 569 lacquer (16% nv)	16	8	0

Table 3 (Continued)

Diluting polymer lacquer (16% nv)						8					16
Percent diluting polymer in the polymer portion of the ink	0					42.5					85
Pigment to binder ratio in ink	0.15					0.15					0.15
Percent solids of ink	18					18					18
Polymer Ratio in the Ink Vehicle - solids											
UCARMAG 569	100	57.5	57.5	57.5	58	57.5	15	15	15	15	15
UCARMAG 527		42.5					85				
VYHH			42.5					85			
VMCH				42.5					85		
VAGH					43					85	
VAGF						42.5					85
Total	100	100	100	100	100	100	100	100	100	100	100

Ink**Properties**

20° Gloss *	84	83	74	100	64	69	2	2	C	2	2
60° Gloss *	99	96	87	99	81	87	17	8	C	17	13

Viscosity cP	65	111	37	190	40	55	14	42	C	57	75
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C=coagulated

It is apparent from Table 3 that UCARMAG 569 lacquer can be used to dilute the pigment concentrate in a wide variety of proportions while maintaining high gloss and low viscosity.

All of the other vinyl lacquers tested could be used at only partial dilutions, and only after first diluting with the UCARMAG 569 lacquer.

The VMCH lacquer may gel in the ink when added at high concentrations, but it can be successfully added at moderate concentrations. In moderate concentrations, it increased ink viscosity, but maintains excellent gloss. UCARMAG 527 which, like VMCH, also contains maleic acid comonomer, showed a similar but less pronounced increase in viscosity, indicating a bridging interaction with the pigment components and the carboxylic acid groups.

Inks prepared from UCARMAG 569 (See Table 3) had very good adhesion to commercially important substrates used in flexible and rigid packaging. Data are shown in Table 4.

The ink prepared using the all UCARMAG 569 based recipe in Table 3 was cast at 18 % solids in MEK using a #12 wire wound rod and allowed to dry. Tape adhesion was tested by using method ASTM D 3359-87 with Scotch brand 610 tape.

Table 4
Adhesion of Formulated ink

<u>Substrate</u>	<u>Adhesion</u>	
Aluminum foil	very good	No removal
Corona treated oriented polypropylene	very good	No removal
Corona treated oriented polyethylene	good	Trace removal after wrinkling
Corona treated oriented polyester	very good	No removal

Inks cast on substrate using No. 12 wire wound rod

Tape test; ASTM D 3359-87 using Scotch brand 610 tape

Table 5 illustrates that UCARMAG 569 could be used successfully with a variety of typical colorants use in the graphic arts industry. All compositions in the series showed low viscosity and brilliant gloss.

Table 5
Polymer 569 / Pigment Concentrates with Various Process Colors

	Pigment Grind		- Parts by Weight	
UCARMAG 569	15	15	15	15
Lithol rubine red (1) *	15			
Pthalo blue-rd (2) *		15		
Pthalo blue-gr (3) *			15	
Diarylide yellow (4) *				15
Methyl ethyl ketone	70	70	70	70
Total Grind	100	100	100	100

Viscosity of Pigment Concentrate cP

100	40	214	437
-----	----	-----	-----

TABLE 5 (CONTINUED)

Properties of Ink (18% nv in MEK) **

60 ° Gloss	99	115	113	141
20 ° Gloss	84	100	103	170

Viscosity cP

65	42	57	59
----	----	----	----

* Sun Chemical

(1) SUNBRITE RUBINE 57:1

(2) SUNFAST BLUE 15:2

(3) SPECTRA PAC E BLUE

15:4

(4) SPECTRA PAC E

YELLOW 14

** 3 parts pigment concentrate diluted with 16 parts of Polymer 569 lacquer in MEK at 16% nv

Cast on polyester film using

#12 ww rod

Although the invention has been described with respect to specific aspects, those skilled in the art will recognize that other aspects are intended to be within the scope of the claims which follow.

- 24 -

CLAIMS:

1. A composition comprising,
 - (a) from about 1 to 99 weight percent, based on the total weight of the composition, of pigment particles; and
 - (b) from about 1 to 99 weight percent, based on the total weight of the composition, of a polymer effective to inhibit the agglomeration of the pigment particles when dispersed in a liquid medium:
characterized in that the polymer is polymerised from a vinyl halide, a vinyl ester and a monomer having a sulfonic acid group or a derivative thereof and is effective to provide a Viscosity Retention Factor of 5 or less.
2. The composition of claim 1 wherein the polymer is effective to provide a Viscosity Retention Factor of 3 or less.
3. The composition of claim 1 wherein the polymer is effective to provide a Viscosity of 700 centipoises or less.
4. The composition of claim 3 wherein the polymer is effective to provide a Viscosity of 200 centipoises or less.
5. The composition of claim 1 wherein the monomer is selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, sulfoethyl methacrylate, sulfomethyl methylacrylate, and mixtures thereof.
6. The composition of claim 1 wherein the composition is a solid.

- 25 -

7. The composition of claim 1 wherein the composition is a dispersion of the pigment particles in the liquid medium.

5 8. The composition of claim 7 wherein the liquid medium is a solvent for the polymer.

9. The composition of claim 7 wherein the liquid medium is a monomer.

10 10. The composition of claim 8 wherein the solvent is an ester or a ketone.

15 11. A coating made from the composition of claim 1.

20 12. A coated substrate comprising a substrate having coated thereon a coating made from the composition of claim 1.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US00/10512 (22) International Filing Date: 19 April 2000 (19.04.00) (30) Priority Data: 60/130,087 20 April 1999 (20.04.99) US (71) Applicant (for all designated States except US): UNION CARBIDE CHEMICALS & PLASTICS TECHNOLOGY CORPORATION [US/US]; 39 Old Ridgebury Road, Danbury, CT 06817-0001 (US). (71)(72) Applicants and Inventors: MAYER, Walter, Paul [US/US]; 6 Shcoolhouse Lane, Lebanon, NJ 08833 (US). BURNS, Richard, Jude [US/US]; 319 De Maria Drive, Easton, PA 18040 (US). FISCO, Matthew, Christopher [US/US]; 9 Summit Road #26, Middlesex County, South River, NJ 08882 (US). HARVEY, James, Richard [US/US]; 53 Stella Drive, Somerset County, Bridgewater, NJ 08807 (US). CLARK, Elke, Monika, Antje [US/US]; 12 Country Club Drive, Hunterdon County, Ringoes, NJ 08551 (US). (74) Agent: PACCIONE, Stanley, J.; Union Carbide Chemicals & Plastics Technology Corporation, 39-Old Ridgebury Road, Danbury, CT 06817-0001 (US).		(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, ID, IL, IN, IS, JP, KR, KZ, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TR, TT, UA, US, UZ, VN, ZA, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PIGMENTED COMPOSITIONS		
(57) Abstract <p>This invention relates to pigment compositions, e.g., pigmented ink and coating compositions, which comprise pigment particles and a polymer. The polymer can be obtained, for example, by the copolymerization of monomers including: (1) a vinyl halide, e.g., vinyl chloride; (2) a vinyl ester, e.g., vinyl acetate; and (3) a monomer having a sulfuric acid group or a derivative thereof, e.g., an acrylate or methacrylate moiety having a sulfonic acid group or a metal or amine salt thereof. The polymer can impart enhanced dispersion property characteristics to the compositions while also having desirable adhesion and rheological characteristics and thermal stability.</p>		

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and the specification of which: ☐ is attached hereto ().
(check one) ☒ was filed on April 19, 2000 as (UC17974-1).
Application No. PCT/US00/10512
and was amended on

(d) I acknowledge my duty under 37 CFR 1.56 to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in 37 CFR 1.56(b). If this application is a continuation-in-part application, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 CFR 1.56(b) that became available between the filing date of the prior application from which priority is claimed in part (f) below, and the national or PCT international filing date of this application.

(e) I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate listed below or § 365(a) of any PCT international application that designated at least one of the United States as a country of entry. I have stated below the filing date of each foreign application for patent or inventor's certificate or any other equivalent PCT international application having a filing date before that of the application on which priority is claimed.

Additional claims for benefit are attached.

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith. Address all correspondence to The Dow Chemical Company's appointed counsel at:



I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under 18 U.S.C. § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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(☒) Additional names and signatures are attached.

Additional names, addresses and signatures to be attached to Form No. 1000

Entitled: **DECLARATION AND POWER OF ATTORNEY**

At: Bound Brook, NJ 08551
 this 15th day of October 2001

Signature: Elke Monika Clark
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 this _____ day of _____ 19____

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 Residence: _____

Country: _____
 Citizenship: _____
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